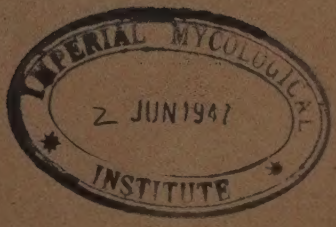
COMPTES RENDUS

(DOKLADY)

DE L'ACADÉMIE DES SCIENCES DE L'URSS

NOUVELLE SÉRIE

1943



VOLUME XXXVIII

№ 9

ÉDITION DE L'ACADÉMIE DES SCIENCES DE L'URSS
MOSCOU

AVIS AUX AUTEURS

Les «Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS» paraissent tous les dix jours. Neuf numéros composent un volume pourvu, d'une table des matières. Il y a quatre volumes par année.

Les «Comptes Rendus de l'Académie des Sciences de l'URSS» en, de courtes communications précisent l'essentiel des travaux en préparation. Ces articles, ne dépassant pas en règle générale quatre pages, sont donnés en anglais ou en français. Ils embrassent les sciences mathématiques, physiques, naturelles et appliquées, mettant au jour les résultats de recherches scientifiques en cours ou qui viennent d'être achevées, et représentant ainsi les plus récentes données de l'investigation scientifique.

L'auteur a droit à 25 exemplaires de son article.

Adressez les manuscrits à la Redaction des «Comptes Rendus», Kazan, rue Baumann, 19.

COMPTES RENDUS

(DOKLADY)

DE L'ACADÉMIE DES SCIENCES DE L'URSS

COMITÉ DE RÉDACTION

A. Arbusov, de l'Académie, **A. Borissiak**, de l'Académie, **V. Chlopin**, de l'Académie, **A. Deborin**, de l'Académie, **A. Fersman**, de l'Académie, **A. Frumkin**, de l'Académie, **A. Kolmogoroff**, de l'Académie (vice rédacteur), **L. Orbeli**, de l'Académie (rédacteur en chef), **A. Richter**, de l'Académie, **S. Soboleff**, de l'Académie, **S. Wawilow**, de l'Académie (vice rédacteur)

NOUVELLE SÉRIE

11-me année

Paraissant tous les dix jours

1943

VOLUME XXXVIII, № 9

TABLE DES MATIÈRES

MATHÉMATIQUES Pages

W. Gontcharoff. Sur la succession des événements dans une série d'épreuves indépendantes répondant au schème de Bernoulli 283

A. A. Popov. A New Method for Grapho-Analytical Integration 286

G. Pfeiffer, Member of the Academy of the Ukrainian SSR. On the Practical Application of the Criteria of Existence of Linear Factors in Symbolic Forms 289

ASTRONOMIE

B. J. Levin. Gaseous resp. Dusty Structure of Comet Tails of Different Types . 292

THÉORIE DE L'ÉLASTICITÉ

V. V. Novojilov. On the Solution of Thin Shell Theory Problems in Stresses and Moments 294

PHYSIQUE

M. Kornfeld. Rigidity Modulus of Liquids and its Dependence on Temperature . 298

PHYSIQUE DU GLOBE

V. L. Ginsburg. On the Anomalies in the Polarization of Twilight 301

CHIMIE

A. G. Bergmann. Simplest Inorganic Glasses on the Base of Calcium Nitrate 304

G. B. Boky and **E. E. Wainstein.** On the Nature of the Chemical Bond in Some Inorganic Compounds 307

Anna Gelman. On the Synthesis of Ethylene Complexes of Platinum with Four Different Substituting Groups in the Inner Sphere 310

CHIMIE PHYSIQUE

G. B. Ravich and **G. G. Tzurinov.** Investigation of the Polymorphism of Trilaurin 314

Édition de l'Académie des Sciences de l'URSS

Moscou 1943

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XXXVIII, № 9

MATHÉMATIQUES

SUR LA SUCCESSION DES ÉVÉNEMENTS DANS UNE SÉRIE D'ÉPREUVES INDÉPENDANTES RÉPONDANT AU SCHÈME DE BERNOULLI

Par W. GONTCHAROFF

(Présenté par A. N. Kolmogoroff, de l'Académte, le 17. XII. 1942)

Supposons qu'on fait une série de n épreuves, dans chacune desquelles peut apparaître ou bien l'événement A ou bien son opposé B. Dans chaque épreuve la probabilité de l'apparition de A soit p, celle de B soit q ($p+q=1$; $0<p,\ q<1$).

Si l'événement A apparaît r fois de suite (et non plus), nous parlerons d'une A-série à r termes; d'une façon analogue seront définies les B-séries à s termes. Dans la série d'épreuves considérée désignons par α_r la quantité de A-séries à r termes et par β_s celle de B-séries à s termes. On a évidemment

$$\sum_r r\alpha_r + \sum_s s\beta_s = n.$$

1°. L'espérance mathématique du nombre de toutes les A-séries est égale à

$$p(nq+p) \sim pqn;$$

l'écart quadratique moyen de la même quantité est égal à $\sqrt{pq}$ pour $n=1$; pour $n \geqslant 2$ il est égal à

$$\sqrt{pq\,[(n-2)\,p^2-(n-3)\,pq+nq^2]} \sim \sqrt{pq\,(p^2-pq+q^2)}\,\sqrt{n}.$$

La probabilité de ce que la série de n épreuves contient exactement m A-séries est égale au coefficient de x^m dans le polynôme $P_n(x)$, défini au moyen de la relation récurrente

$$P_n(x) = (p+q)\,P_{n-1}(x) - pq\,(1-x)\,P_{n-2}(x); \quad P_0(x)=1; \quad P_1(x)=q+px.$$

2°. L'espérance mathématique du nombre de toutes les A-séries et de toutes les B-séries ensemble est égale à

$$2npq + (p^2+q^2) \sim 2pqn;$$

l'écart quadratique moyen de cette quantité est nul pour $n=1$, et égale

$$\sqrt{2pq\,[2\,(p^2-pq+q^2)\,n-(3p^2-4pq+3q^2)]} \sim 2\sqrt{pq\,(p^2-pq+q^2)}\,\sqrt{n}$$

pour $n \geqslant 2$.

3°. L'espérance mathématique du nombre de A-séries à r termes est p^r pour $n=r$, et égale

$$p^r q\,[(n-r+1)\,q+2p] \sim p^r qn$$

pour $n \geqslant r+1$; le carré de l'écart quadratique moyen de cette quantité est

$$\begin{cases} p^r(1-p^r) & \text{pour } n=r, \\ p^r q\,[(n-r+1)\,q+2p]\,\{1-p^r q\,[(n-r+1)\,q+2p]\} & \text{pour } r+1 \leqslant n \leqslant 2r, \\ \text{idem} + 2p^{2r}q & \text{pour } n=2r+1; \end{cases}$$

enfin pour $n \geqslant 2r+2$ il égale

$$p^r q\,\{qn+[2p-(r-1)\,q]\}+p^{2r}q^2\,\{-[(2r+1)\,q-2p]\,qn+[2p^2-4\,(2r+1)\,pq+ \\ +(3r^2-1)\,q^2]\} \sim p^r q^2\,\{1-p^r q\,[(2r+1)\,q-2p]\}\,n.$$

4°. L'espérance mathématique du nombre de A- et B-séries à r termes (sommairement) égale

$$\begin{cases} s_r & \text{pour } n=r, \\ K_1 n + K_0 & \text{pour } n \geqslant r+1, \end{cases}$$

où l'on pose

$$s_r = p^r + q^r \quad (r=1, 2, \ldots),$$
$$K_1 = pq\,(s_{r-1}-s_r), \quad K_0 = pq\,[(r+1)\,s_r-(r-1)\,s_{r-1}];$$

le carré de son écart quadratique moyen est

$$\begin{cases} s_r - s_r^2 & \text{pour } n=r, \\ (K_1 n+K_0)-(K_1 n+K_0)^2 & \text{pour } r+1 \leqslant n \leqslant 2r-1, \\ \text{idem} + 4p^r q^r & \text{pour } n=2r, \\ \text{idem} + 2\,(pqs_{r-1}s_r + p^r q^r) & \text{pour } n=2r+1; \end{cases}$$

enfin pour $n \geqslant 2r+2$ il est égal à

$$M_1 n + M_0 \sim M_1 n$$

avec

$$M_1 = p^2q^2\,\{-(2r+1)\,s_{r-1}^2+4\,(r+1)\,s_{r-1}s_r-(2r+3)\,s_r^2\}+pq\,(s_{r-1}-s_r)+2p^{r+1}q^{r+1},$$
$$M_0 = pq\,\{3\,(r^2-1)\,pqs_{r-1}^2+2\,[1-(r+1)\,(3r+1)\,pq]\,s_{r-1}s_r- \\ -[2-(r+1)\,(3r+5)\,pq]\,s_r^2\}+2p^r q^r-4rp^{r+1}q^{r+1}.$$

5°. Toutes les valeurs considérées obéissent à la limite à la loi de Gauss.

6°. Considérons encore la longueur de la A-série maximale. La probabilité $P_m^{(n)}$ de ce que le nombre de ses termes ne surpasse pas m est donnée par la formule

$$\frac{1+O(p^m)}{[(1+qp^{m+1}+O(p^m)]^{n+1}}+O(mp^n).$$

Il en suit que pour $n \to \infty$ l'espérance mathématique de la longueur maximale est asymptotiquement égale à

$$\frac{\lg n}{\lg \frac{1}{p}}$$

et que

$$P^{(n)}_{\left[\frac{\lg n}{\lg \frac{1}{p}}\right]+\lambda} \sim e^{-qp^{\lambda+1-\theta_n}},$$

θ_n désignant la partie fractionnaire de $\dfrac{\lg n}{\lg \frac{1}{p}}$.

Aussi la différence entre la longueur maximale d'une A-série et l'entier du nombre $\frac{\lg n}{\lg \frac{1}{p}}$ n'obéit elle pas à la limite à une loi de distribution déterminée: il se trouve bien qu'il existe un ensemble infini de lois limites (de «points de condensation»); ces lois sont naturellement en échelle, dépendent d'un paramètre qui varie d'une façon continue et sont données par la formule

$$F_\alpha(t) = e^{-qp^{\lambda+\alpha}} \quad \text{pour} \quad \lambda < t < \lambda+1;\ \lambda = \ldots, -2, -1, 0, 1, 2, \ldots$$
$$[0 \leqslant \alpha \leqslant 1;\quad F_1(t) \equiv F_0(t+1)].$$

Comme on voit, les lois $F_\alpha(t)$ ne sont pas du type gaussien: on les pourrait nommer «deux fois exponentielles».

On obtient tous les résultats énoncés le plus simplement par la considération de la fonction génératrice

$$F\begin{pmatrix} x_1, x_2, \ldots \\ y_1, y_2, \ldots \end{pmatrix} \equiv \sum p_{\substack{\alpha_1\alpha_2\ldots \\ \beta_1\beta_2\ldots}} x_1^{\alpha_1} x_2^{\alpha_2} \ldots y_1^{\beta_1} y_2^{\beta_2} \ldots$$

où par $p_{\substack{\alpha_1\alpha_2\ldots \\ \beta_1\beta_2\ldots}}$ est désignée la probabilité de ce que dans la série $\sum_r r\alpha_r + \sum_s s\beta_s$ des épreuves il se trouve α_1 A-séries à un terme, α_2 A-séries à deux termes etc., ensuite β_1 B-séries à un terme, β_2 B-séries à deux termes et ainsi de suite.

Il se trouve que

$$-F\begin{pmatrix} x_1, x_2, \ldots \\ y_1, y_2, \ldots \end{pmatrix} = \frac{\left(1 + \sum_r p^r x_r\right)\left(1 + \sum_s q^s y_s\right)}{1 - \sum_r p^r x_r \sum_s q^s y_s}.$$

Manuscrit reçu
le 17. XII. 1942.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XXXVIII, № 9

MATHEMATICS

A NEW METHOD FOR GRAPHO-ANALYTICAL INTEGRATION

By A. A. POPOV

(Communicated by A. N. Kolmogoroff, Member of the Academy, 13. XII. 1942)

1. Fundamentals. If $f(x)$ is a function given in a graphical form in the interval l, and $\varphi(x)$ — a function, continuous and singlevalued, given in an analytical form, then the integral

$$I = \int_0^l f(x)\,\varphi(x)\,dx \tag{1}$$

can be represented in the form

$$I = f\int_0^l \varphi(x)\,dx = f\Omega, \tag{2}$$

where

$$f = \frac{I}{\Omega} = \frac{\int_0^l f(x)\,\varphi(x)\,dx}{\int_0^l \varphi(x)\,dx}, \tag{3}$$

Ω is the area bounded by curve $\varphi(x)$ and the axis of abscissae.

Denote by F the point situated over the centre of gravity of the area Ω at the height f above the axis of the abscissae (Fig. 1).

Then, if the position of the point F, to which we assign the name of singular focal point, and the area Ω are known, it will be easy to find the integral I.

2. Fundamental Theorem. The singular focal point can easily be found by a purely graphical method, based on a fundamental theorem. This theorem I shall give without proof.

Suppose that a given curve $f(x)$ (Fig. 2) is in the intervals l_1 and l_2 replaced approximately by two straight lines; then

$$f\Omega = f_1\Omega_1 + f_2\Omega_2; \tag{4}$$

f_1 is the ordinate of the point F_1 located over the centre of gravity of the area Ω_1, and f_2 is the ordinate of the point F_2 located over the centre of gravity of the area Ω_2.

It is a simple matter to show that point F is located on the straight line drawn between points F_1 and F_2.

From the above-said it follows that the position of F and, consequently, of its ordinate f can be easily found if the position of the centres of gravity of the shaded areas is known.

3. Application of the Fundamental Theorem. In Fig. 3 we will indicate all the operations connected with the determination of the position of F* when the interval l is divided into four equal parts, within which the curve $f(x)$ is approximately a straight line.

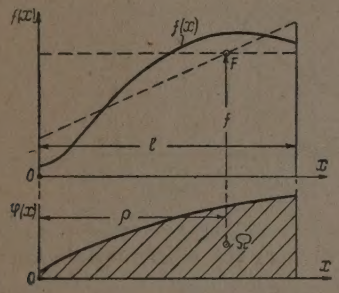


Fig. 1.

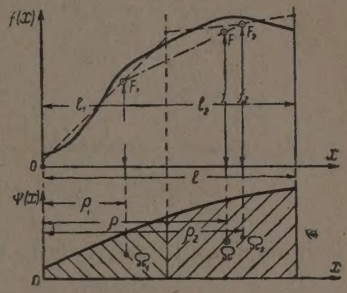


Fig. 2.

For a definite function $\varphi(x)$ it is possible, by dividing the interval l into m parts ($m=1, 2, 4, 8, 16, \ldots$), to compute the position of the centre of gravity, and to plot a scale ** which is said to be a functional scale. In Fig. 3 this scale is represented with the indication of the order in which the points F_1, F_2, F_3 and F_4 are connected.

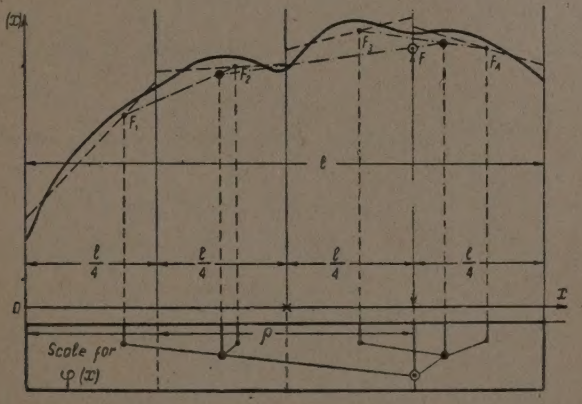


Fig. 3.

It is also possible by means of such a construction to represent the value of the integral

$$\int_0^x f(x)\,\varphi(x)\,dx \qquad (5)$$

in the form of a plot—the integral curve.

---

* We examine the case when $\varphi(x)=x^2$.

** Such scales have been constructed by the author for $\varphi(x)=x$, x^2, x^3, x^4 (computation of moments) and for a number of other cases.

Such a curve is plotted in Fig. 4.

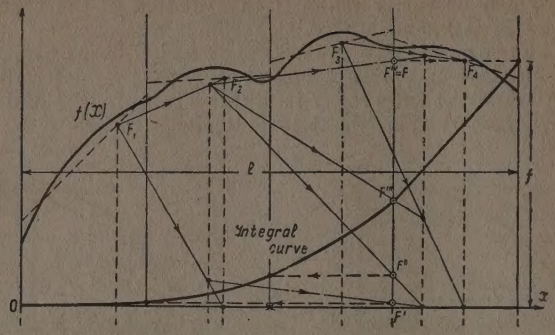


Fig. 4.

If it is required to derive from the curve $\psi(x)$ the «differential» curve

$$\frac{\frac{d\psi(x)}{dx}}{\varphi(x)},$$

the opposite construction to that given in Fig. 4 can be applied.

Received
13. XII. 1942.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XXXVIII, № 9

MATHEMATICS

ON THE PRACTICAL APPLICATION OF THE CRITERIA OF EXISTENCE OF LINEAR FACTORS IN SYMBOLIC FORMS

By G. PFEIFFER, Member of the Academy of the Ukrainian SSR

Any symbolic form of n-th power of $n+k$ variables can be reduced to the canonical aspect

$$\left.\begin{aligned} \Omega_n \equiv M dx_1 \dots dx_n + \sum_{\sigma_1 \tau_1}^{kn} M_{\tau_1}^{\sigma_1} dx_1 \dots dx_{\tau_1 - 1} dz_{\sigma_1} dx_{\tau_1 + 1} \dots dx_n + \\ + \sum_{\sigma_1 \sigma_2 \tau_1 \tau_2}^{kn} M_{\tau_1 \tau_2}^{\sigma_1 \sigma_2} dx_1 \dots dx_{\tau_1 - 1} dz_{\sigma_1} dx_{\tau_1 + 1} \dots dx_{\tau_2 - 1} dz_{\sigma_2} dx_{\tau_2 + 1} \dots dx_n + \dots, \\ M \not\equiv 0. \end{aligned}\right\} \quad (1)$$

Suppose that the form (1) possesses a linear factor

$$\omega \equiv a_1 dz_1 + \dots + a_k dz_k - b_1 dx_1 - \dots - b_n dx_n. \quad (2)$$

The coefficients b cannot become zero simultaneously; the existence of the factor

$$\tilde{\omega} \equiv a_1 dz_1 + \dots + a_k dz_k \quad (3)$$

would, owing to the identity

$$\Omega_n \tilde{\omega} \equiv 0 \quad (4)$$

and to the non-identity

$$M \not\equiv 0, \quad (5)$$

lead to the impossible equalities

$$a_1 = a_2 = \dots = a_k = 0. \quad (6)$$

Let us assume that

$$b_n \not\equiv 0 \quad (7)$$

and that

$$\Omega_n \equiv \Omega_{n-1} dx_n + \bar{\Omega}_n \quad (8)$$

(dx_n did not enter either into Ω_{n-1} or into $\bar{\Omega}_n$).

The factor ω (2) could be found by the well known criterion

$$\Omega_n \omega \equiv 0, \quad (9)$$

which leads to a series of dependent relations, as well as by a simpler one, established by the author in his preceding paper([1]) and giving no supefluous relations,

$$\Omega_{n-1}\omega \equiv -\, b_n \Omega_n . \tag{10}$$

If to the form Ω_n there belong ρ multipliers

$$\omega_1, \omega_2, \ldots, \omega_\rho, \qquad \rho \leqslant n, \tag{11}$$

it can be supposed that this form contains the factors

$$\left.\begin{gathered} \tilde{\omega}_1, \tilde{\omega}_2, \ldots, \tilde{\omega}_\rho, \\ (\tilde{\omega}_j \equiv a_1^j dz_1 + \ldots + a_k^j dz_k - b_1^j dx_1 - \ldots - b_n^j dx_n) \\ \rho \leqslant n \end{gathered}\right\}. \tag{12}$$

[or, what is the same, the factor

$$\eta_1 \tilde{\omega}_1 + \eta_2 \tilde{\omega}_2 + \ldots + \eta_\rho \tilde{\omega}_\rho \tag{13}$$

($\eta_1, \ldots, \eta_\rho$ being arbitrary coefficients)], possessing the property

$$\left.\begin{aligned} & b_n^\rho \neq 0, && (14_1) \\ & b_{n-1}^{\rho-1} \neq 0, \ b_n^{\rho-1} = 0, && (14_2) \\ & \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ & b_{n-\rho+1}^1 \neq 0, \ b_{n-\rho+2}^1 = 0, \ \ldots, \ b_n^1 = 0 && (14_\rho) \end{aligned}\right\} \tag{14}$$

Let us prove the following theorem:

Theorem. *The expressions*

$$\left.\begin{aligned} & \eta_1 \tilde{\omega}_1 + \eta_2 \tilde{\omega}_2 + \ldots + \eta_{\rho-1} \tilde{\omega}_{\rho-1}, && (15_1) \\ & \eta_1 \tilde{\omega}_1 + \eta_2 \tilde{\omega}_2 + \ldots + \eta_{\rho-2} \tilde{\omega}_{\rho-2}, && (15_2) \\ & \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ & \eta_1 \tilde{\omega}_1 + \eta_2 \tilde{\omega}_2 && (15_{\rho-2}) \\ & \eta_1 \tilde{\omega}_1 && (15_{\rho-1}) \end{aligned}\right\} \tag{15}$$

are factors of the forms

$$\Omega_{n-1}, \ \Omega_{n-2}, \ \ldots, \ \Omega_{n-\rho+2}, \ \Omega_{n-\rho+1}, \tag{16}$$

determined by the relations

$$\left.\begin{aligned} & \Omega_n \equiv \Omega_{n-1} dx_n + \overline{\Omega}_n , \\ & \Omega_{n-1} \equiv \Omega_{n-2} dx_{n-1} + \overline{\Omega}_{n-1} , \\ & \ldots\ldots\ldots\ldots\ldots\ldots \\ & \Omega_{n-\rho+2} \equiv \Omega_{n-\rho+1} dx_{n-\rho+2} + \overline{\Omega}_{n-\rho+2} . \end{aligned}\right\} \tag{17}$$

One writes these forms directly without having to seek them.

In fact, the expression (13) is the factor of the form Ω_n

$$\Omega_{n-1} (\eta_1 \tilde{\omega}_1 + \ldots + \eta_{\rho-1} \tilde{\omega}_{\rho-1} + \eta_\rho \tilde{\omega}_\rho) \equiv -\, \eta_\rho b_n^\rho \Omega_n , \tag{18}$$

but there is

$$\Omega_{n-1} \tilde{\omega}_\rho \equiv -\, b_n^\rho \Omega_n ; \tag{19}$$

therefore

$$\Omega_{n-1} (\eta_1 \tilde{\omega}_1 + \ldots + \eta_{\rho-2} \tilde{\omega}_{\rho-2} + \eta_{\rho-1} \tilde{\omega}_{\rho-1}) \equiv 0. \tag{20}$$

The expression (15_1) is the factor of the form Ω_{n-1}

$$\Omega_{n-2}(\eta_1\tilde{\omega}_1 + \ldots + \eta_{\rho-2}\tilde{\omega}_{\rho-2} + \eta_{\rho-1}\tilde{\omega}_{\rho-1}) \equiv -\eta_{\rho-1}b_{n-1}^{\rho-1}\Omega_{n-1}, \tag{21}$$

but there is

$$\Omega_{n-2}\tilde{\omega}_{\rho-1} \equiv -b_{n-1}^{\rho-1}\Omega_{n-1}; \tag{22}$$

therefore

$$\Omega_{n-2}(\eta_1\tilde{\omega}_1 + \ldots + \eta_{\rho-2}\tilde{\omega}_{\rho-2}) \equiv 0. \tag{23}$$

The expression (15_2) is the factor of the form Ω_{n-2}:

$$\Omega_{n-3}(\eta_1\tilde{\omega}_1 + \ldots + \eta_{\rho-2}\tilde{\omega}_{\rho-2}) \equiv -\eta_{\rho-2}b_{n-2}^{\rho-2}\Omega_{n-2}, \tag{24}$$

and so forth.

Moreover, the equalities (17) lead to the following thesis.

Thesis. The factor ω having the property (14_ρ) is a multiplier of the form Ω_n, if it is a multiplier of the coefficients in the decomposition of the form Ω_n to the linear combination of the products of all dz and of the groups of differentials

$$dx_{n-\rho+1},\ dx_{n-\rho+2},\ \ldots,\ dx_n. \tag{25}$$

Received
17. XI. 1942.

REFERENCES

[1] G. Pfeiffer, C. R. Acad. Sci. URSS, XXXVIII, No. 8 (1943).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XXXVIII, № 9

ASTRONOMY

GASEOUS RESP. DUSTY STRUCTURE OF COMET TAILS OF DIFFERENT TYPES

By B. J. LEVIN

(Communicated by S. I. Wawilow, Member of the Academy, 22. XII. 1942)

According to S. V. Orlov (1), comet tails of the I type consist of gases, while those of the II and III types are dusty structures. The gaseous nature of the I type of tails, as clearly brought forth by spectroscopic investigations, stands beyond any doubt. No less certain is the dusty nature of comet tails of the III type, though there are no spectrograms of such tails. Matter is quite different, however, as to the tails of the II type.

The mechanical theory of cometary forms contains evidence o fthe effect that tails of the II type are syndynamics whose repulsing accelerations $1+\mu$ range within 0.5—2.5. About the same repulsing accelerations were obtained for separate clouds of CN and C_2, as had been observed for the head of Halley's comet (1910 II). In these cases when the emanation of CN could be traced at a sufficiently long distance from the nucleus, they were found to penetrate into the tails of the II type. In comets displaying a sufficiently intense Nλ-radiation the latter could also be observed in tails of the II type.

A spectrum taken with prismatic cameras even at a short distance from the comet's head is found to be continuous, though frequently showing an anomalous energy distribution. On the other hand, in spectrograms of tails of the I type the spectrum at some distance from the head also becomes gradually continuous, which is certainly due to mutual superposition of monochromatic images of the tail which grows broader, the farther from the head. This is also due to the fact that we have to do not with a line spectrum, but with a band spectrum. The comparison of spectrograms of one and the same comet taken with different prismatic cameras has shown that in the case of high dispers on the spectrum becomes discontinuous at a greater distance from the head. The existence of a discontinuous spectrum, far from being firmly established for tails of the II type, is thus questionable.

A decisive rôle in the problem of the nature of tails of the II type thus belongs to the question as to the light pressure and to the possibility quantitatively to explain the repulsive accelerations observed.

Debye (2), having applied the general theory of diffraction on a globe, elaborated by G. Mi, suggested formulae for light pressure upon globules of arbitrary material and made calculations for some particular cases. Orlov, making use of Debye's data for totally reflecting particles and taking account of energy distribution in the solar spectrum, has found $1+\mu$ for particles of various dimensions. The good agreement of the maximum value of $1+\mu$ obtained in the course of this calculation, as well as the maximum value of $1+\mu$ observed in tails of the II type, were interpreted as an evidence in favour of their dusty nature. As a matter of

fact, the agreement is no significant one, since the data used pertain to idealized spheres of total reflection. Contrary to this, powdery particles of cometary tails should be supposed to be stony structures and thereby endowed with optical properties approaching those of dielectrics.

According to Debye's data, I have calculated the values of $1+\mu$ for transparent (dielectric) particles with an index of refraction $n=1.5$ and $n=2$, and for absorbing(metallic) particles with $m=1.57(1-i)$ (see table). The densities of the particles δ were put equal to 3, 4 and 6 g/cm^3, respectively. Energy distribution in the solar spectrum was adopted from Lindblad ([3]) (averaged data by Abbot and Wilsing).

For particles with $n=1.5$ the maximum value of $1+\mu$ is equal to 0.5. Even for particles with $n=2$ it does not exceed 1.2, i. e. is appreciably lower than that observed in cometary tails of the II type. It is known, on the other hand, that minerals that make up the largest part of rocks of the earth crust an of meteorites, have refraction indices ranging from 1.5 to 1.6. Thus, light pressure upon stone particles may well account for the repulsive accelerations $1+\mu<0.5-0.7$, which are common for tails of the III type, whereas it cannot possibly account for accelerations as high as $1+\mu=2.5$, which are observed in tails of the II type. Small absorbing particles can scarcely suffer repulsive accelerations as high as this either, being endowed with greater density than stone particles. Besides, the assumption that the cometary nucleus disintegrates into metallic dust is absolutely inadequate.

r in mμ	$1+\mu$		
	$n=1.5;\ \delta=3$	$n=2;\ \delta=4$	$m=1.57(1-i);$ $\delta=6$
50	0.05	0.3	1.7
100	0.3	1.0	1.5
150	0.5	1.2	—
200	0.5	1.2	—
300	0.5	0.7	—
400	0.4	0.5	—

It should not be supposed, however, that particles with $1+\mu>1$ are never to be observed in tails of the III type. While investigating the main tail of the comet 1901 I (a synchronic of the III type, at the moment of formation, May 2.65 of the universal time), Moisseev ([4]) found, on a photograph taken on May 6, the top of the tail (very short at that time) to contain particles with $1+\mu=1.72$, and on photographs taken on May 11 and 20, with $1+\mu=0.77$ and 0.89, respectively. Particles that are more subject to Sun repulsion have by this time already been scattered in the space.

As for tails of the II type, they should be considered. in accordance with spectroscopic data, as consisting of the same gases as the envelope of the head of the comet. Bobrovnikov's hypothesis based on the reconstruction of CN molecules, when passing from the head into a tail of the I type, into CO and N_2 should be discarded as unneccesary. CN and C_2 molecules, if present in a sufficient quantity, form tails of the II type, and if they are few—envelopes of the cometary head only, penetrated with jets of molecules forming tails of the I type. The idea that the head and the tail are rather independent formations superimposed one upon another has been suggested by Balde and adopted by Wurm who has suggested a series of photographs of comets to illustrate this assumption. As may be seen from the above-said, this is true with regard to tails of the I type alone.

Received
10.XII.1942.

REFERENCES

[1] С. В. Орлов, Кометы (1935). [2] P. Debye, Ann. d. Phys., 4, 30, 57 (1909). [3] Handb. der Astrophys., VI, 26 (1929). [4] П. Д. Моисеев, Астр. журн., II, № 1, 73 (1925).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XXXVIII, № 9

THEORY OF ELASTICITY

ON THE SOLUTION OF THIN SHELL THEORY PROBLEMS IN STRESSES AND MOMENTS

By V. V. NOVOJILOV

(Communicated by B. G. Galerkin, Member of the Academy, 24. VII. 1942)

1. Making use of Kirchhoff's hypothesis and neglecting magnitudes of order t/R in comparison with unity, one may obtain the following set of formulae in the general theory of thin shells:

a) Equilibrium equations for an element of the shell:

$$\left.\begin{aligned}
&\frac{1}{AB}\left\{\frac{\partial BT_1}{\partial\alpha}+\frac{\partial AS}{\partial\beta}+\frac{\partial A}{\partial\beta}S-\frac{\partial B}{\partial\alpha}T_2\right\}+N_1/R_1+\overline{X}=0\\
&\frac{1}{AB}\left\{\frac{\partial BS}{\partial\alpha}+\frac{\partial AT_2}{\partial\beta}-\frac{\partial A}{\partial\beta}T_1+\frac{\partial B}{\partial\alpha}S\right\}+N_2/R_2+\overline{Y}=0\\
&\frac{1}{AB}\left\{\frac{\partial BN_1}{\partial\alpha}+\frac{\partial AN_2}{\partial\beta}\right\}-T_1/R_1-T_2/R_2+\overline{Z}=0\\
&\frac{1}{AB}\left\{\frac{\partial BM_1}{\partial\alpha}+\frac{\partial AH}{\partial\beta}+\frac{\partial A}{\partial\beta}H-\frac{\partial B}{\partial\alpha}M_2\right\}-N_1=0\\
&\frac{1}{AB}\left\{\frac{\partial BH}{\partial\alpha}+\frac{\partial AM_2}{\partial\beta}-\frac{\partial A}{\partial\beta}M_1+\frac{\partial B}{\partial\alpha}H\right\}-N_2=0,
\end{aligned}\right\}\qquad(1)$$

b) The relation between stresses, moments and deformations of the middle surface:

$$\left.\begin{aligned}
&T_1=\frac{Et}{1-\mu^2}(\varepsilon_1+\mu\varepsilon_2);\quad T_2=\frac{Et}{1-\mu^2}(\varepsilon_2+\mu\varepsilon_1);\quad S=\frac{Et}{2(1+\mu)}\omega,\\
&M_1=D(\varkappa_1+\mu\varkappa_2);\quad M_2=D(\varkappa_2+\mu\varkappa_1);\quad H=D(1-\mu)\tau.
\end{aligned}\right\}\qquad(2)$$

c) Deformations of the middle surface in terms of its displacement:

$$\left.\begin{aligned}
&\varepsilon_1=\frac{1}{A}\frac{\partial u}{\partial\alpha}+\frac{1}{AB}\frac{\partial A}{\partial\beta}v+\frac{w}{R_1};\quad \varkappa_1=\frac{1}{A}\frac{\partial\vartheta}{\partial\alpha}+\frac{1}{AB}\frac{\partial A}{\partial\beta}\psi;\\
&\varepsilon_2=\frac{1}{B}\frac{\partial v}{\partial\beta}+\frac{1}{AB}\frac{\partial B}{\partial\alpha}u+\frac{w}{R_2};\quad \varkappa_2=\frac{1}{B}\frac{\partial\psi}{\partial\beta}+\frac{1}{AB}\frac{\partial B}{\partial\alpha}\vartheta;\\
&\omega=\frac{A}{B}\frac{\partial}{\partial\beta}\left(\frac{u}{A}\right)+\frac{B}{A}\frac{\partial}{\partial\alpha}\left(\frac{v}{B}\right);\\
&\tau=\frac{1}{2}\left\{\frac{A}{B}\frac{\partial}{\partial\beta}\left(\frac{\vartheta}{A}\right)+\frac{B}{A}\frac{\partial}{\partial\alpha}\left(\frac{\psi}{B}\right)-\right.\\
&\qquad\left.-\frac{1}{BR_1}\left(\frac{\partial u}{\partial\beta}-\frac{1}{A}\frac{\partial B}{\partial\alpha}v\right)-\frac{1}{AR_2}\left(\frac{\partial v}{\partial\alpha}-\frac{1}{B}\frac{\partial A}{\partial\beta}u\right)\right\};\\
&\vartheta=-\frac{1}{A}\frac{\partial w}{\partial\alpha}+\frac{u}{R_1};\quad \psi=-\frac{1}{B}\frac{\partial w}{\partial\beta}+\frac{v}{R_2}.
\end{aligned}\right\}\qquad(3)$$

It is well to linger on the curious history of torsion strains of the middle surface τ. In his fundamental work on the theory of shells ([1]) where the subject is set forth differently from the text-book ([2]), A. Love gives for torsion the formula referred to above, and reproaches his fore-runner Aron ([3]) for having given a formula lacking symmetry with respect to u and v. Later on, in his text-book ([2]) A. Love, without any argument, omitted from his formulae some terms which, generally speaking, are not essential terms, but whose omission breaks the symmetry of the formula.

So he exposed himself to — and actually received from N. Kilchevsky ([4]) and A. Goldenweiser ([5]) — the very same reproach which he had formerly addressed to Aron. Arguing against Love, Goldenweiser used the same formula which about fifty years ago had served Love as an argument against Aron.

2. Note that in the formula for τ the underlined terms are not usually essential and can be neglected. Then the following simplified expression is obtained for torsion:

$$2\tau = \frac{B}{A}\frac{\partial}{\partial\alpha}\left(\frac{\psi}{B}\right) + \frac{A}{B}\frac{\partial}{\partial\beta}\left(\frac{\vartheta}{A}\right). \tag{4}$$

If τ be determined by formula (4), the system of equations (1), after (2) is substituted in it and account is taken of the expressions (3), may be written thus:

$$\left.\begin{aligned}
&\frac{Et}{1-\mu^2}\left\{\frac{1}{A}\frac{\partial\Omega}{\partial\alpha} - \frac{1-\mu}{2B}\frac{\partial\vartheta}{\partial\beta} + (1-\mu)\,\vartheta/R_2\right\} + N_1/R_1 + \overline{X} = 0\\
&\frac{Et}{1-\mu^2}\left\{\frac{1}{B}\frac{\partial\Omega}{\partial\beta} + \frac{1-\mu}{2A}\frac{\partial\vartheta}{\partial\alpha} + (1-\mu)\,\varphi/R_1\right\} + N_2/R_2 + \overline{Y} = 0\\
&\frac{1}{AB}\left\{\frac{\partial BN_1}{\partial\alpha} + \frac{\partial AN_2}{\partial\beta}\right\} - T_1/R_1 - T_2/R_2 + \overline{Z} = 0\\
&D\left\{\frac{1}{A}\frac{\partial\Phi}{\partial\alpha} - \frac{1-\mu}{2B}\frac{\partial\Psi}{\partial\beta} + (1-\mu)\frac{\vartheta}{R_1R_2}\right\} - N_1 = 0\\
&D\left\{\frac{1}{B}\frac{\partial\Phi}{\partial\beta} + \frac{1-\mu}{2A}\frac{\partial\Psi}{\partial\alpha} + (1-\mu)\frac{\psi}{R_1R_2}\right\} - N_2 = 0.
\end{aligned}\right\} \tag{5}$$

Here the following notations are introduced:

$$\begin{aligned}
\Omega &= \frac{1}{AB}\left\{\frac{\partial Bu}{\partial\alpha} + \frac{\partial Av}{\partial\beta}\right\} + \left(\frac{1}{R_1} + \frac{1}{R_2}\right)w,\\
\vartheta &= \frac{1}{AB}\left\{\frac{\partial Bv}{\partial\alpha} - \frac{\partial Au}{\partial\beta}\right\},\\
\Phi &= \frac{1}{AB}\left\{\frac{\partial B\vartheta}{\partial\alpha} + \frac{\partial A\psi}{\partial\beta}\right\},\\
\Psi &= \frac{1}{AB}\left\{\frac{\partial B\psi}{\partial\alpha} - \frac{\partial A\vartheta}{\partial\beta}\right\}.
\end{aligned}$$

To this shape the equations of the theory of thin shells were first transformed by W. Sokolovsky ([6]) (relative to the particular case of a spherical shell).

3. The use of the equations of the theory of shells in that form proves expedient in many cases and permits in a simple manner to obtain some interesting results.

Thus, applying (5) to a spherical shell and then excluding N_1 and N_2 from the system, by first substituting them from the first two equations in the third one, and afterwards from the two last equations in the third one, one can at once reduce the calculation of spherical shell to the solution of a system of but two equations with two unknowns, Ω and Φ.

This auxiliary system was first deduced by Repman ([7]) in a different way. He, however, owing to the use of unsuitable curvilinear coordinates, overlooked

many possibilities and, besides, in one place of his deduction used the wrong sign, which resulted in an error in his ultimate equations.

Further, system (5) can be successfully used in conjunction with equations (1) for deducing auxiliary equations in the theory of symmetrical deformation of a shell of a revolution body of constant thickness. The advantage of such a deduction over the usual one is that the free term in the auxiliary equation is obtained directly (without any additional transformations) in a rather simple form, instead of the cumbersome form it takes when the current method is used. So far nobody appears to have paid attention to the available possibilities of its simplification.

Limitation of space precludes my entering into detail concerning the above-mentioned useful consequences of using the system (5). But it is hoped that for a qualified reader the indications made will be sufficient. Below another application of the system (5) to the problem of computation of shells in stresses and moments is considered.

4. Starting from system (5), three relations can easily be obtained which, when added to equation (1), will make it possible to solve the problems of the theory of shells not only in terms of displacements, but also in stresses and moments. Thus, from the first two equations of system (5) we at once have:

$$\frac{Et}{1-\mu^2}\left\{\Delta(\Omega)+\frac{1-\mu}{AB}\left[\frac{\partial}{\partial\alpha}\left(\frac{B\vartheta}{R_2}\right)+\frac{\partial}{\partial\beta}\left(\frac{A\psi}{R_1}\right)\right]\right\}+$$
$$+\frac{1}{AB}\left[\frac{\partial}{\partial\alpha}\left(\frac{B}{R_1}N_1\right)+\frac{\partial}{\partial\beta}\left(\frac{A}{R_2}N_2\right)\right]+\frac{1}{AB}\left[\frac{\partial}{\partial\alpha}(B\overline{X})+\frac{\partial}{\partial\beta}(A\overline{Y})\right]=0,$$

where the symbol $\Delta(\ )$ denotes the operation:

$$\Delta(\ )=\frac{1}{AB}\left\{\frac{\partial}{\partial\alpha}\left[\frac{B}{A}\frac{\partial(\ )}{\partial\alpha}\right]+\frac{\partial}{\partial\beta}\left[\frac{A}{B}\frac{\partial(\ )}{\partial\beta}\right]\right\}.$$

As

$$\frac{\partial}{\partial\alpha}\left(\frac{B\vartheta}{R_2}\right)+\frac{\partial}{\partial\beta}\left(\frac{A\psi}{R_1}\right)=\frac{\varkappa_1}{R_2}+\frac{\varkappa_2}{R_1},$$

we can by means of the formulae connecting the stresses and moments with the deformations of the middle surface, rewrite the above formula in the form

$$\frac{12}{t^2}\left\{\frac{1}{R_2}(M_1-\mu M_2)+\frac{1}{R_1}(M_2-\mu M_1)\right\}+\Delta(T_1+T_2)+$$
$$+\frac{1+\mu}{AB}\left[\frac{\partial}{\partial\alpha}\left(\frac{B}{R_1}N_1\right)+\frac{\partial}{\partial\beta}\left(\frac{A}{R_2}N_2\right)\right]+\frac{1+\mu}{AB}\left[\frac{\partial}{\partial\alpha}(B\overline{X})+\frac{\partial}{\partial\beta}(A\overline{Y})\right]=0. \quad (6)$$

This relation between stresses and moments cannot be obtained from system (1) without using the formulae connecting the stresses and moments with deformations. Therefore the above relation may be regarded as a condition of continuity of deformations. The two other conditions will be set in an approximate form.

Experience in solving problems of the theory of shells shows that in the two last equations of system (5) a series of terms may be omitted, without leading practically to an appreciable error. Namely, these equations may be written as follows:

$$N_1=D\frac{1}{A}\frac{\partial\Phi}{\partial\alpha},\quad N_2=D\frac{1}{B}\frac{\partial\Phi}{\partial\beta}.$$

The application of these simplifications to such shells, as the circular, cylindrical or spherical shells, bears out the lawfulness of this method. It may therefore be expected that it will prove to be valid for at least a sufficiently wide circle of problems.

Taking into account the relation between Φ and the moments M_1 and M_2 we have

$$\left.\begin{aligned}(1+\mu)N_1 &= \frac{1}{A}\frac{\partial(M_1+M_2)}{\partial\alpha},\\ (1+\mu)N_2 &= \frac{1}{B}\frac{\partial(M_1+M_2)}{\partial\beta}.\end{aligned}\right\} \qquad (7)$$

The latter relations, which precisely coincide with the corresponding relations of the theory of plates, can be considered as conditions for deformations of the middle surface. Unlike the relations (6) which exactly correspond to the fundamental system of formulae (1), (2), (3), (4), the relations (7) differ from those formulae in involving the neglect of some more terms and an additional error. It is true, they could be deduced in strict correspondence with the formulae (1), (2) and (3), but not without loosing much of their simplicity through the introduction of a series of small terms. From the practical point of view this complication is not expedient. Examining the formulae (6) and (7) in conjunction with equations (1), we shall have a system of eight equations in partial derivatives, and it is to its solution that under given boundary conditions the computation of the shell is reduced.

In conclusion I wish to point out the fact that the accurate expressions of the conditions of continuity of deformations have been deduced by A. Goldenweiser([5],[8]).

Received
24. VII. 1942.

REFERENCES

[1] A. E. H. Love, Phil. Trans. Roy. Soc., **179**, ser. A (1888). [2] A. E. H. Love, A Treatise on the Math. Theory of Elasticity, Cambridge (1934). [3] Aron, Journ. für reine u. ang. Math., **78** (1874). [4] Н. Кильчевский, Прикл. мат. и мех., **2**, вып. 4 (1939). [5] А. Гольденвейзер, сб. «Пластинки и оболочки» (1939). [6] W. Sokolovsky, C. R. Acad. Sci. URSS, XVI, No. 1 (1937). [7] Ю. Репман, сб. «Пластинки и оболочки» (1939). [8] А. Гольденвейзер, Прикл. мат. и мех., **4**, вып. 2 (1940).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XXXVIII, № 9

PHYSICS

RIGIDITY MODULUS OF LIQUIDS AND ITS DEPENDENCE ON TEMPERATURE

By M. KORNFELD

(Communicated by A. F. Joffe, Member of the Academy, 27. XI. 1942)

1. Liquids are known to possess fluidity along with tangential elasticity. The latter is practically unnoticeable against the background of fluidity when the liquid is subject to slow deformations. On the other hand, under a rapidly acting external force the elasticity manifests itself to a full extent, whereas fluidity plays but a subordinate part ([1-3]).

In an attempt to express this fact quantitavely, Maxwell ([4]) has assumed that the shearing deformation, arising in a liquid under the action of external forces, can be represented as a sum of a viscous and an elastic component

$$\Delta_{\text{eff}} = \Delta_{\text{visc}} + \Delta_{\text{elast}}.$$

From this, assuming the viscous deformations to obey Newton's law, and the elastic deformations to be governed by Hooke's law, we directly obtain:

$$\frac{d\Delta_{\text{eff}}}{dt} = \frac{\sigma}{\eta} + \frac{1}{G}\frac{d\sigma}{dt}, \tag{1}$$

where σ is stress; η, viscosity; G, rigidity modulus.

The applicability of this relation to real liquids hat not yet been subjected to experimental verification. The more tempting is the possibility of the existence of substances that would fit within as simple a theoretical scheme. Such substances would be a convenient subject in dealing with some problems of liquid state, and, in particular, useful as a starting point in the investigation of complex amorphous bodies (polymers, gels, clays, etc.).

2. Equation (1) has the most simple solution under a harmonic regime of stress. Putting $\sigma = \sigma_0 e^{i\omega t}$, it is easily seen upon integration that $\Delta = \Delta_0 e^{i(\omega t - \vartheta)}$. We have here also

$$\left.\begin{aligned} \operatorname{tg}\vartheta &= \frac{G}{\omega\eta} \\ G_{\text{eff}} &= \frac{\sigma_0}{\Delta_0} = G\cos\vartheta. \end{aligned}\right\} \tag{2}$$

From the relations (2) it follows that with $\omega \gg \frac{G}{\eta}$ a liquid behaves as a solid body possessing Hooke's rigidity modulus G. Contrary to this, with $\omega \ll \frac{G}{\eta}$ the effective modulus of rigidity G_{eff} is very small, and the properties of the liquid are defined by Newton's viscosity η. In the case of interme-

diate frequencies we have to deal with an «elastico-viscous» body, whose mechanical properties are characterized by the time of relaxation, that is by the ratio $\frac{\eta}{G}$, and whose behaviour depends upon the frequency of the external force.

An experimental method to be published elsewhere (5) permits to measure the effective modulus of rigidity G_{eff} and the angle of phase displacement between the deformation and stress θ. If these two quantities are known, the viscosity and the modulus of rigidity can be easily found:

$$\eta = \frac{G_{\text{eff}}}{\omega \sin \theta}, \quad G = \frac{G_{\text{eff}}}{\cos \theta}. \tag{3}$$

Maxwell's scheme can be considered to be true if it turns out that η and G thus defined do not depend upon ω, and, besides, if the numerical values of viscosity coincide with the usual viscosimetrical data.

3. For the object of investigation I have used rosin which, as had been shown by preliminary experiments (6), fits the most closely into the scheme of Maxwell.

The measurements of G_{eff} and θ were made at frequencies of 2.8×10^3, 1.3×10^5 and 2.9×10^5 Hertz within a temperature interval of -5 to $+70°$ (see table).

Length of specimen in cm	Temperature in °C	G_{eff} in 10^{10} dyne/cm²	θ
$\nu = 2.8 \times 10^3$			
5.7	−6.5	1.17	—
	0	1.16	—
	8.5	1.13	—
	19.0	1.11	—
5.2	21.5	1.11	—
	26.5	1.03	—
	35.5	0.99	—
	40.0	0.87	—
	45.5	0.81	—
3.35	34.5	0.95	—
	36.5	0.90	—
	41.0	0.85	—
	46.5	0.78	4
	48.0	0.72	6
	52.5	0.64	12
	56.5	0.56	14
	58.0	0.46	20
	60.0	0.38	26
2.05	61.5	0.27	44
	63.5	0.24	36
	64.0	0.21	44
	67.0	0.15	40
	69.0	0.12	38

Length of specimen in cm	Temperature in °C	G_{eff} in 10^{10} dyne/cm²	θ
$\nu = 1.3 \times 10^5$			
0.087	22.5	1.11	—
	38.0	0.89	—
	40.0	0.84	—
	43.0	0.82	—
	50.0	0.69	—
	53.0	0.66	—
	56.5	0.64	—
0.051	59.0	0.39	0.5
	61.5	0.37	1.5
	64.5	0.34	3.0
$\nu = 2.9 \times 10^5$			
0.025	19.5	1.07	—
	39.0	0.85	—
	48.5	0.72	—
	55.0	0.64	—

Viscosimeter

Temperature in °C	η in poises	Temperature in °C	η in poises
56.5	1.3×10^6	68.5	4.75×10^4
58.5	1.06×10^6	72.5	2.0×10^4
61.0	3.0×10^5	—	—
64.0	1.55×10^5	—	—

In Figs. 1 and 2 the values of rigidity modulus and viscosity are plotted on the basis of the tabulated data by means of the relations (3). Moreover, in the second of these figures there are given values of viscosity obtained directly with the help of an ordinary rotational viscosimeter.

The results of the experiments, thus represented, show in the first place that in the region of frequencies and temperatures investigated the behaviour of the rosin fits well within the frame of Maxwell's scheme. It is seen further that the

rigidity modulus in the case of rosin essentially depends upon temperature, decreasing as the latter increases. This circumstance necessitates the introduction of some corrections in our conceptions of the «melting» of amorphous bodies. So far it was customary to look upon the modulus of rigidity as independent of temperature and to explain the softening of amorphous bodies on heating entirely by their decrease in viscosity. Thereby the rigidity modulus of ordinary low viscous liquids was assigned values of a magnitude of 10^{10} dyne/cm², just as in the case of solid bodies, and the time of relaxation was estimated as $10^{-10} \times 10^{-12}$ sec. Fig. 1 shows,

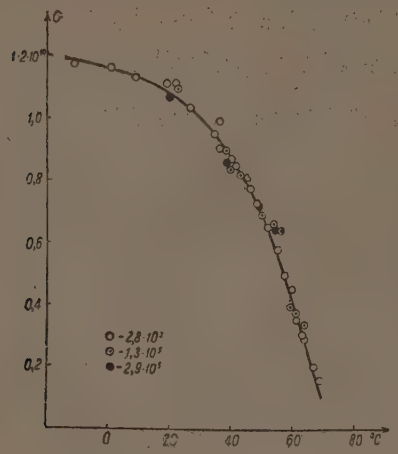


Fig. 1.

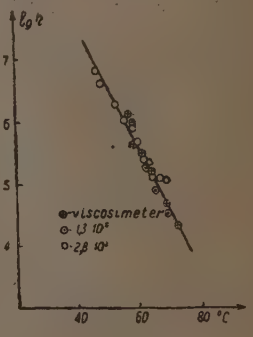


Fig. 2.

however, that for some liquids their modulus of rigidity is certainly below 10^{10} dyne/cm². Naturally enough, these liquids will behave as solid bodies at relaxation times, greatly exceeding the relaxation time mentioned above; their state will be like that of a rubber or jelly. Other experiments with rosin are underway, which, being carried on at higher temperatures (within a viscosity interval of 10^5 to 10^2 poises) have already furnished confirmation to this point of view.

The author is indebted to P. L. Kapitza, who has provided the facilities for carrying out this work and payed constant attention to it.

Leningrad Physical-Technical Institute.
Institute for Physical Problems.
Academy of Sciences of the USSR.

Received
27.XI.1942.

REFERENCES

[1] J. G. Maxwell, Proc. Roy. Soc., No. 148 (1873). [2] S. Petralia, Nuovo Cimento, **17**, 478 (1940). [3] M. Kornfeld and M. Ryvkin, Journal of Phys. USSR, **1**, 183 (1940). [4] J. G. Maxwell, Phil. Trans., **157**, 52 (1866). [5] М. Корнфельд, ЖЭТФ, вып. 3—4 (1943). [6] M. Kornfeld, Bull. Acad. Sci. URSS, sér. phys.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XXXVIII, № 9

GEOPHYSICS

ON THE ANOMALIES IN THE POLARIZATION OF TWILIGHT

By V. L. GINSBURG

(Communicated by S. I. Wawilow, Member of the Academy, 22. XII. 1942)

Within the last years I. A. Khvostikov and others ([1-3]) carried out measurements of the polarization of twilight at the zenith. In the course of these measurements it was found that the dependence of the degree of polarization upon the height of the sun is no monotonous one, but shows several maxima and minima. The position of these maxima and minima, as well as the rest of details in the shape of the curve, vary according to the day; the first deep minimum, however, lies invariably within the region of 75—100 km*.

It has been suggested ([1]) that polarization anomalies are directly associated with the presence in the stratosphere of ionized layers, an that the decrease in the polarization of light scattered by these layers is due to a sharp increase in the anisotropy of the ions, as compared to neutral particles. The author finds this interpretation unacceptable. Making any reasonable assumption as to the structure of the atmosphere, the number of molecules per 1 cm^3 at an altitude of 100 km proves no less than 10^{14} ([5]). If we were to assume that the properties of the Heaviside layer E were due to ions rather than to electrons, which is not safely established yet, the ion concentration is found not to exceed the value 1.5×10^{10} ([5,6]). Moreover, the polarizability of the ions as to the order of their magnitude is similar to that of neutral particles. Hence it is obvious that the light scattered by the ions of the E layer makes up no more than about $^1/_{10\,000}$ of the total light scattered in this region; consequently, irrespective of the coefficient of ion anisotropy, it cannot possibly call forth the effects observed. It should also be noted that there is scarcely any reason to suppose that ion anisotropy materially exceeds that of atoms or molecules: the anisotropy of ions may well be either below or above that of neutral particles (compare, e. g., the anisotropy of H_2 and H_2^+). At altitudes $\sim$200—400 km the number of ions whose concentration does not exceed $\sim10^{10}$ may prove comparable to the total number of particles. However, the suggestions made above, as well as the presence of polarization anomalies at lower altitudes, and some other reasons** make us renounce to this interpretation as a fundamental one.

---

* To a given heigt of the sun, i. e. to its depression, there corresponds a definite height of the atmosphere layer, stattering the main part of the solar light ([1, 4]), and this is the figure suggested above.

** Whereas the presence in the F layer of a large number of ions ($\sim10^{10}$) has not been proved directly and merely does not contradict radioobservations, it has been firmly established that the number of free electrons in this region amounts to $3\cdot10^6$ per cm^3. Electrons scatter light without polarizing it, and their effect in the visible part of the spectrum is 300—400 that of the molecules of O_2 or N_2.

It appears thus impossible to associate the polarization anomalies observed at twilight to the anisotropy of molecules*. And this conclusion is no casual one, since anisotropy plays subordinate part in the whole complex of problems connected with sky luminescence, and can by no means account for the most typical and important phenomena in this field, viz. absence and position of neutral points, distribution of polarization all over the sky according to the height of the sun, to various perturbations and to changes in polarization ([7],[8]). As the main factor responsible for the normal polarization phenomena should be considered the multiple scattering of solar light in the atmosphere; as a rule, it is practically sufficient to take into account along with the one time scattering, double scattering alone([7],[9]). An important, and sometimes the main part is played by scattering on coarse particles in the atmosphere (dust, water drops), as well as by the reflection of sun light from the surface of the earth. This is why, according to measurements made by Khvostikov and others, the polarization of the sky light in the zenith, the height of the sun being $h \cong 0°$, does not exceed 70% and often amounts to 40—50% only; in this case if we were to take into account the anisotropy alone, this would lead to $p = 91\%$ as a value for polarization ([9]). The polarization of the luminescence of the sky during twilight has been studied more than once, but largely for small depressions of the sun ($h \sim -5°$). Besides the unmonotony of the variation of p in the zenith [see([7]), p. 113)], a variation in the distance of the neutral points of Babinet and Arago from the sun and the antisolar point, respectively, is observed to take place with decreasing h. For great sun depressions the position of neutral points was determined by Dorno ([8]); to begin with a sun height of $h = -4°$, the point of Arago begins rapidly, sometimes by leaps, to approach the zenith. With $h > -6°$ the point of Babinet behaves in an analogous way. Dorno reports a case when the position of these points was observed up to a value $h = -11°$ (the height of the layer illuminated by the sun in the zenith being $\sim$120—140 km). The distance of the points of Arago and Babinet from the antisolar point and the sun, respectively, made up 35° and 70°, whereas with $h = 0°$ these distances were equal to about 18—20°. Such a behaviour of the neutral points makes still more obvious the peculiar character of the polarization phenomena during twilight. In their observations pertaining to the zenith, Khvostikov, Rosenberg and others availed themselves of technical means which made it possible to trace the polarization practically up to the close of the astronomical twilight. As may clearly be seen from the above-said, these interesting variations cannot and should not be considered separately from the whole problem of polarization of sky luminescence during twilight. In the process of these studies it would be of special interest to trace up to the close of twilight the variations in the position of neutral points and in the polarization at an angle of 90° to the sun rays.

The existing theory of polarization of the sky light ([9]) deals directly with the case of positive heights of the sun alone. In order to account for the normal course of polarization during twilight it is but natural to make an attempt to take into account the secondary light scattering, which has not been made as yet**. It should be noted that in the course of the twilight there may take place redistribution of density in the atmosphere (pulsating atmosphere), changes in the density gradient***, air streams, etc. Dynamical processes of this kind must tell upon changes in the polarization and in the intensity of the light scattered ([4], [10]). Moreover,

---

*More strictly speaking, variations of the atmosphere with altitude (variation in the contents of different gases, dissociation of oxygen molecules, ions, electrons) and the variation in anisotropy connected herewith, may lead to a change in polarization with altitude, though to a considerably smaller one that experimentally observed at altitudes $\sim$100 km.

** A sharp variation of polarization with altitude usually observed up to an altitude of $\sim$100 km ([2]), points, if viewed from this angle, to a higher importance of multiple scattering. It must be followed by an increase in the blue part of the light scattered, which is observed experimentally ([11]).

*** For instance, the gradient of electron concentration of electrons in the F layer is known to vary sharply during twilight ([6]). This process may be not only a static one, but a dynamic as well, i. e. it may prove to be connected with redistribution of the density of the atmosphere.

polarization may be affected by meteoric dust, which may be present in considerable amounts at altitudes $\sim 100-150$ km (4). Scattering of light on coarse particles, as is said above, has a sharp effect upon the polarization of sky light, since, on the one hand, scattering on coarse particles is strongly depolarized, and, on the other hand, it is very intense; for instance, a particle with the dimensions $\sim 10^{-5}$ cm scatters light of nearly the same intensity as $10^{17}-10^{18}$ molecules, since, until the wave-length exceeds the dimensions of the particle, the intensity of the light scattered by the former is to the intensity of light scattered by a molecule approximately as $\left(\frac{V}{v}\right)$, where V is the volume of the particle and v that of the molecule ($v-\alpha \sim 2 \times 10^{-24}$, where α is the polarizability of the molecule).

In the course of the day polarization processes are strongly dependent on the solar activity and on the conditions of illumination of the given region of earth surface by the sun (7). There is no reason to suppose that these factors play a less important part during twilight. As the state of the ionosphere is also dependent on solar radiation, the existence of a correlation between polarization and the state of the ionosphere is quite natural (2). The rotation of the polarization plane at high altitudes, which has been observed by Rosenberg (3), as well as the rotation of the polarization plane during solar eclipses (12), stand in need of special explanation and further experimental study. It should be noted that the cases of rotation of the polarization plane observed pertain to regions in the neighbourhood of neutral points or, at any rate, to regions with low polarization, where the rôle of multiple scattering and of various secondary effects is of particular importance. The possibility of the rotation observed being due to fluorescent luminescence of the atmosphere, excited either by solar radiation or by electronic impact*, cannot yet be rejected (12, 13). In fact, in both cases (3, 11), the part played by fluorescence, which is generally no important one, may become essential. However, the stock of experimental evidence on the subject being rather scanty, it would be premature to suggest any final conclusion as to the causes of rotation.

P. N. Lebedev Physical Institute.
Academy of Sciences of the USSR.

Received
22. XII. 1942.

REFERENCES

[1] I.A. Khvostikov and A. N. Sevchenko, C. R. Acad. Sci. URSS, XIII (4).347 (1936); И. А. Хвостиков, УФН, **19**, 183 (1938). [2] V. M. Bovcheverov and oth., Bull. Acad. Sci. URSS, sér. géophys., 657 (1940); C. R. Acad. Sci. URSS, XXVI, 897 (1940). [3] G. V. Rosenberg, ibid., XXXVI, 288 (1942). [4] Н. М. Штауде, Фотометрич. наблюдения сумерек, изд. АН СССР (1936). [5] А. Н. Щукин, Физич. основы распространения радиоволн в ионосфере (1940). [6] H. Rukop, Elektrot. Nachr. Technik, **10** (1932). [7] Ch. Jensen, Handb. d. Phys., **19**, 105 (1928); Meteorol. ZS, **49**, 419 (1932). [8] C. Dorno, Physik d. Sonnen und Himmelsstrahlung, 67—82 (1919). [9] Y. Y. Tichanowsky, Phys. ZS., **28**, 252, 680 (1927); **29**, 442 (1928). [10] В. Г. Фесенков, Астр. журнал, **7**, в. 2 (1930); A. V. Mironov, Bull. Acad. Sci. URSS, sér. géophys., 843 (1940). [11] I. A. Khvostikov, E. N. Magid and A. A. Shubin, ibid. 675 (1940). [12] W. Cohn, Phys. Rev., **45**, 848 (1934). [13] J. Cabannes et H. Garrique, C. R., **203**, 484 (1936).

* Polarization of luminescence due to impact differs from that of scattered light. Besides, the rotation of the plane of fluorescence polarization may be due to the influence of the terrestrial magnetic field, and to disturbances of normal illumination conditions (changes in the direction of sun rays as a result of refraction, etc.).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XXXVIII, № 9

CHEMISTRY

SIMPLEST INORGANIC GLASSES ON THE BASIS OF CALCIUM NITRATE

By A. G. BERGMANN

(Communicated by V. G. Chlopin, Member of the Academy, 16. XII. 1942)

Nitrates belong to salts remarkable for their simplicity: equilibria with such salts are very clear and reached very rapidly both in the molten state and in solutions. Molten nitrates give most mobile melts at comparatively low temperatures. All of this is evidence that the inner structure of crystalline nitrates, of their solutions and melts is not complex and that, in particular, autocomplex formation is absent.

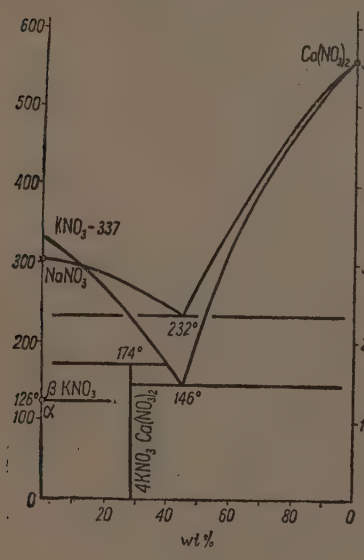


Fig. 1.

In this light special interest is due to Rostkovsky[1], in this laboratory having established the formation of glasses in the system KNO_3—$Na(NO_3)_2$, in which, owing to the appearance of the compound $4KNO_3 \cdot Ca(NO_3)_2$, melts of very low melting point are formed. The eutectic crystallizes at 146°, its composition being 54.2% KNO_3 and 45.8% $Ca(NO_3)_2$ (by weight). The transition point corresponds to 174°, the composition being 60% KNO_3 and 40% $Ca(NO_3)_2$ (by weight) (Fig. 1). In the ternary system consisting of calcium, potassium and sodium nitrates, investigated by the author and P. I. Protzenko, there has been discovered area of the formation of such melts as are easily converted into glass. This area is expressed by the field of primary crystallization of the compound $4KNO_3 \cdot Ca(NO_3)_2$ and of the adjoining sections of the fields of the components. The eutectic crystallization is lowered to 133°. The ternary transition point corresponds to 160° and 53.9% KNO_3, 29.4% $Ca(NO_3)_2$ and 16.7% $NaNO_3$ (by weight) (Fig. 2).

The glasses obtained were stable at room temperature for several years. At higher temperatures their crystallization sets in. The glasses show a characteristic «conchoidal» fracture. They differ from ordinary glasses by their marked hygroscopicity which is due to the presence of calcium nitrate. In another lateral system $Ca(NO_3)_2$—$NaNO_3$ there is a simple eutectic at 232° and 54.9% $NaNO_3$ (by weight) (Fig. 1). No compound is formed between the components.

It is characteristic that in the systems $Ba(NO_3)_2$—KNO_3 ([2], [3]) and $Ba(NO_3)_2$—$NaNO_3$ ([3]), in which there is no formation of complexes, absolutely no viscosity, or glass forming ability is observed; and so, too, in the ternary system $Ba(NO_3)_2$—KNO_3—$NaNO_3$ investigated by V. P. Radischev.

In the ternary system $Sr(NO_3)_2$—KNO_3—$NaNO_3$, according to the preliminary investigations of our collaborators, although there is a somewhat greater viscosity compared to the system with $Ba(NO_3)_2$, yet neither a formation of complexes on the surface, nor glass formation could be established.

It is very characteristic that in the system with zinc chloride $ZnCl_2$—KCl—NaCl([4]) a reverse phenomenon is observed. Zinc chloride, melting at 318°, gives viscous melts when potassium or sodium chlorides are added to it, the latter forming a series of complex compounds $2ZnCl_2 \cdot KCl$, $2ZnCl_2 \cdot 3KCl$, $ZnCl_2 \cdot 2KCl$

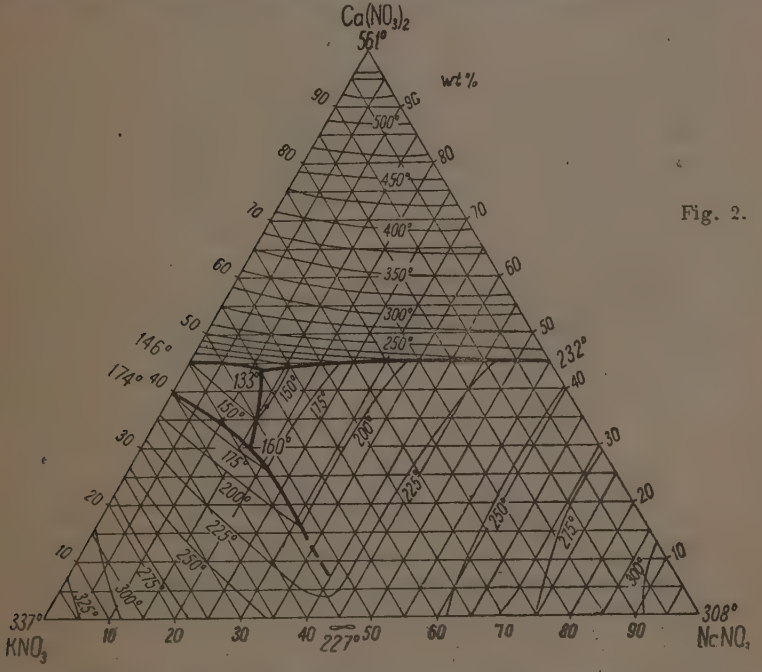


Fig. 2.

and $ZnCl_2 \cdot 2NaCl$. Viscosity decreases sharply: thus, the viscosity of $ZnCl_2$ at 400° equals 1.590 poises and that of the eutectic mixtures from 0.045 to 0.052 poises, i. e. 30 times less.

Apparently, in this case complicated autocomplexes of zinc chloride, giving viscous salts, are converted into melts of less complicated molecular structure which are complex compounds of zinc chloride mentioned above.

The results of the study of the systems $Ca(NO_3)_2$—KNO_3—$NaNO_3$ and $ZnCl_2$—KCl—NaCl, showing such opposite manifestations of viscosity, which, indeed reflect in a very representative manner the molecular rearrangements taking place in the molten state, unquestionably are of great theoretical interest. They call for further, more profound investigation that would take account of a series of physical-chemical properties: specific weight, viscosity, electroconductivity, surface tension, specific heat, etc. Another interesting point about these two ternary systems is that because of the low melting point of the components and particularly of the melts [the eutectic in the systems $Ca(NO_3)_2$—KNO_3—$NaNO_3$ is at 133°, and in the system $ZnCl_2$—KCl—NaCl, at 202, 206 and 216°C] the conversion from aqueous systems to melts can be easily realized, owing to the light solubility of the salts, particularly of $ZnCl_2$ and $Ca(NO_3)_2$.

The investigations of aqueous solutions demonstrated that barium and potassium nitrates form (which they do not in the case of melts) a non-congruent compound $Ba(NO_3)_2 \cdot KNO_3$ (5).

Calcium and potassium nitrates in aqueous solutions call forth a reciprocal increase of solubility. Frowein (6) on the base of the data obtained by Barbaudy(7) at 30° and his own data at 0° and 20° expressed the opinion that a double salt was formed in the solution.

An investigation of the specific weight and viscosity of the system $Ca(NO_3)_2$—KNO_3 has been carried out by E. R. Natzalishvili and A. G. Bergmann in an interval stretching from 430° to the outset of crystallization, and by V. D. Poliakov(9) for KNO_3—$NaNO_3$ in the area of supercooled melts and below the crystallization curve (135°). The electroconductivity in the molten state has been investigated by E. R. Natzalishvili and A. G. Bergmann for the systems $Ca(NO_3)_2$—$(KNO_3)_2$ and $Ca(NO_3)_2$—$NaNO_3$, and by A. G. Bergman, V. D. Poliakov and I. M. Chagin for the system KNO_3—$NaNO_3$ (8, 9).

The investigation of the viscosity demonstrated that in the system calcium nitrate—potassium nitrate viscosity in the area of glass formation increases to extremely high values, this having not been observed in the system $Ca(NO_3)_2$—$NaNO_3$. The curves of electroconductivity for the melts of calcium and potassium nitrates show the formation of one minimum coinciding with the ordinate of the compound $4KNO_3 \cdot Ca(NO_3)_2$. With a rise of the temperature the minima become less definite and are shifted towards the component, with lower values for the properties [$Ca(NO_3)$], this having been demonstrated previously (8) for system with a well marked maximum upon the melting diagram. In the present system it was for the first time that the formation of minima was established for systems, in the constitution diagram of which there is a compound with a hidden maximum. The author and his collaborators are engaged in the further development of this problem.

Received
16. XII. 1942.

REFERENCES

[1] А. П. Ростковский, Ж. Р. Химич. общ., **62**, 2055 (1930). [2] Clark and Harkins, Journ. Am. Chem. Soc., **37**, 1816 (1915). [3] А. П. Ростковский, ЖОХ, IV (1934). [4] I. N. Nikonova, S. P. Pavlenko and A. G. Bergmann, Bull. Acad. Sci. URSS, sér. chim. (1941). [5] H. W. Foote, Amer. Chem. Journ., **32**, 251 (1904). [6] Frowein, ZS. f. anorg. allg. Chem., **169**, 336 (1928). [7] Barbaudy, Rec. trav. chim. Pays-Bas, **42**, 638 (1923). [8] A. G. Bergmann and I. M. Chagin, Bull. Acad. Sci. URSS, sér. chim., 727 (1940). [9] V. D. Poliakov, ibid., No. 3 (1941).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XXXVIII, № 9

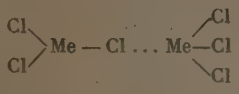
CHEMISTRY

ON THE NATURE OF THE CHEMICAL BOND IN SOME INORGANIC COMPOUNDS

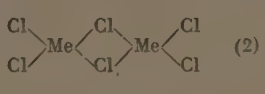
By G. B. BOKY and E. E. WAINSTEIN

(Communicated by V. G. Chlopin, Member of the Academy, 5. XII. 1942)

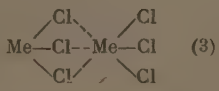
§ 1. At present it is possible to designate a whole class of chemical compounds that find no satisfactory explanation on the basis of classical notions on valency developed by Kossel, Lewis and Sidjwick. In the explanation of the nature of bonds in some polymer halides, complex oxides, boron hydrides, carbonyl compounds etc. until now there is neither clearness, nor uniformity, nor even synonymousness. Thus, for instance, following Werner (3), for halides of trivalent elements formulae of at least the following three kinds should be accepted as equally probable:



(1)



(2)



(3)

An objective criterion for the writing down of the structural formula of such a compound is offered by the method of X-ray analysis.

Among compounds of the type $[MeCl_3]_2$ the structure of the dimer $(AlCl_3)_2$ was studied with particular care by Ketelaar who used the X-ray method. It was found out that the lattice of $(AlCl_3)_2$ was a molecular one. The atoms of aluminium were situated in the structure in pairs in the octahedric voids formed by compactly packed chlorine atoms. The coordination number for aluminium equals 4: the second atom of Al and 3 Cl atoms. The form of the coordination polyhedron is a slightly distorted tetrahedron. The distance Cl—Cl in the tetrahedron approximately corresponds to the sum of the ionic radii of chlorine, the distance Al — Al is 0.64Å. It is above four times less than the sum of the atomic radii of Al (2.84 Å), and almost two times less than the sum of the ionic radii ($2\,Al^{+++} = 1.14$Å). The distance 0.64 Å is the more astonishing, because, if it were the consequence of the decrease of distance between the three times charged iones Al^{3+}, it would be difficult to imagine what forces might affect the very strong electrostatic repulsion of the aluminium ions. These particular properties of $[AlCl_3]_2$ are in sharp contradiction with the facts that were to be expected on the basis of the hypothetic structures of this compound, to which one is led by the conceptions of Werner.

As a second example of the abnormal proximity of metallic atoms in structures one can cite the structure studied shortly by Boky, Ussikov and Trussevich (1) of the compound $PtNH_3C_2H_4Cl_2$-*cis* synthesized by Gelman (4). In this compound

which, according to crystallochemical data, proved to be a dimer, the distance Pt—Pt which equals 1.4 Å is also less than the sum of atomic radii (2.75 Å) and of ionic ones of bivalent platinum (1.6 Å) and is just a little above the sum of ionic radii for tetravalent platinum (1.32 Å). The coordination number of platinum in this compound equals 6, this being characteristic, generally speaking, for tetravalent platinum. The form of the coordination polyhedron is a slightly distorted octahedron. The nearest neighbours of platinum in the structure are the second atom of platinum, ammonia, two chlorine atoms and two carbon atoms.

In the compound of aluminium and platinum examined above the abnormally small distance between the metals suggests the presence of a chemical bond between them. In both compounds all the exterior valency electrons are already used for the formation of monomers and therefore other electrons should be attracted to participate in the formation of a bond between the metallic atoms.

§ 2. Pauling ([3]) has achieved a satisfactory congruence between stereochemical peculiarities of the structure of compounds and the symmetry of the wave functions of the electrons, realizing the bond. Thus, if the wave functions of the electrons involved in the formation of the bond are d^2sp^3, then the structure of the compound formed is an octahedron; if the number d of functions equals 4, the sixtuple orientation is realized in the form of a trigonal prism; if these functions are d^3s or sp^3, tetrahedron is formed; finally, to the combination of functions dsp^2 corresponds a square. Vast experimental material confirms the rules expressed above, thus making it possible to admit the justice of an inverse conclusion.

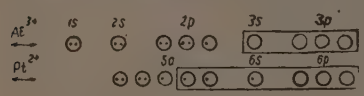


Fig. 1.

If in the compounds discussed above ($[AlCl_3]_2$ and $[PtNH_3C_2H_4Cl_2]_2$) a chemical bond is supposed to exist between the metallic atoms (we shall call it «intravalent» or «dimetallic» bond), owing to participation of deeper lying electrons, we arrive at a scheme (see figure) that makes it possible to explain many peculiarities of structure and the properties of such compounds. This scheme expresses the distribution of the electrons according to the energetic groups in aluminium and platinum in the compounds $[AlCl_3]_2$ and $[PtNH_3C_2H_4Cl_2]_2$.

The «orbites» on which the bond of Al and of Pt, correspondingly, with the neighbouring atoms is realized, are indicated in the schemes by rectangular frames.

§ 3. The proposed scheme of the interaction of metallic atoms in the compounds $[AlCl_3]_2$ and $[PtNH_3C_2H_4Cl_2]_2$ makes it possible to understand a series of remarkable properties of such compounds.

a) The fact that the deeper laying $2p$-electrons of Al or 5 d-electrons of Pt are involved into the bond leads to a more intense interaction between the two metallic atoms of the dimers, with the result that the distance between the centres of gravity of these atoms in the compounds is decreased. This circumstance, obvious by itself, can be supported to a certain degree by comparing the observed abnormally small distances Al—Al with the quantum-mechanical evaluations of this quantity. Using the methods of Slater ([10]) and Pauling ([9]), we obtained for aluminium the value $(\sqrt{\overline{r^2}})_{Al} = 0.35$ Å instead of 0.32 Å obtained by Ketelaar experimentally; and for platinum 0.71 Å instead of 0.7Å.

b) We shall indicate yet the similarity of the valence state of Al in $[AlCl_3]_2$ with the usual valence state of silicon, stated a long time ago by W. Vernadsky ([2]) in aluminosilicates. A similar valence state should be expected for the other elements of the IIIb subgroup, particularly for boron.

c) The dipole moment of the monomer $AlCl_3$ ([12]) approximately equals 5.4×10^{-18} CGSE. If one supposes that the dimer is formed at the expense of dipole forces, the dipole moment of the dimer should be in any case above this value, the formation of a quadrupole being impossible owing to steric hindrance. If the proposed scheme is just, compensation of the charges should be complete and the dipole moment of the compound should equal zero. And actually the latter is the case ([11]).

d) The opinion expressed here concerning the structure of the dimer $(AlCl_3)_2$ makes it possible perhaps to rise in another way the question about the reasons for the catalytic activity of aluminium chloride. $(AlCl_3)_2$ dissociates into monomers, having a «free» valence. Such monomers should be very near in their properties to radicals and therefore highly reactive.

e) A. Gelman (4) in 1939 made an attempt to explain the structure of the compound $PtNH_3C_2H_4Cl_2$, considering it as a monomer. This point of view, which by the way has already called forth serious objections from Keller (6), is in contradiction with the X-ray structural data and has some principal defects connected with the impossibility of making a difference between the two carbon atoms in ethylene. The interpretation of the structure of $PtNH_3C_2H_4Cl_2$ as that of a dimer allows a better explanation of the similarity of chemical behaviour between the platinum in that compound and tetravalent platinum, observed and experimentally supported by Gelman and Riabchikov (5). According to classical ideas, Pt should be bivalent in this compound.

As for the strong *trans*-influence of the group C_2H_4, pointed out by Gelman, the study of the structure having demonstrated that ethylene is situated in the plane perpendicular to the one in which are all the other atoms, this compels to consider the mechanism of such a phenomenon as obscure and in any case differing from the corresponding influence of acid groups.

§ 4. The «dimetallic» bond can be sometimes identified with the usual covalent bond between two metallic atoms, as for instance is the case with calomel. The observed decrease of distance between the mercury atoms in the structure of Hg_2Cl_2 and the diamagnetism of this compound are quite in agreement with the idea of the existence of a bond between the atoms of mercury. As applied to compounds of the type Al_2Cl_6 (Al_2F_6, B_2H_6 and others), that are also diamagnetic, the existence of double bond between the metallic atoms does not seem improbable. In all the cases when the introduction of a dimetallic bond can be expedient, a decisive part should be played by the measurements of intraatomic intervals and the estimation of steric relationship. Thus, the short distance between the metals in the structures $(AlCl_3)_2$ and $(PtNH_3C_2H_4Cl_2)_2$ observed experimentally, allows in no case the use of chlorine atoms as intermediate links of the bond which is customary(7) in generally accepted schemes for the structure of such compounds. In this case the «intravalent» bond becomes absolutely necessary for explaining the stability of the compound.

Institute of General and Inorganic Chemistry
and Biogeochemical Laboratory.
Academy of Sciences of the USSR.

Received
5. XII, 1942.

REFERENCES

[1] G. Boky, P. Ussikov and G. Trussevich, Bull. Acad. Sci. URSS, sér, chim., № 6 (1942). [2] В. И. Вернадский и С. Курбатов, Земные силикаты (1937). [3] Вернер, Новые воззрения в области неоргапич. химии (1936). [4] A. Gelman, C. R. Acad. Sci. URSS, XXIV, 551 (1939); XVI, 359 (1937). [5] A. Gelman and D. Riabchikov, ibid., XXXIII, № 7—8 (1941). [6] R. Keller, Chem. Rev., 28, 229 (1941). [7] G. Morgan and F. H. Burstall, Inorganic Chemistry, 92 (1938). [8] L. Pauling, Nature of the Chemical Bond (1940). [9] L. Pauling, Proc. Roy. Soc. London, 27 (A), 114, 181 (1927). [10] I. Slater, Phys. Rev., 26,57 (1930). [11] Смайс, Диэлектрическая постоянная структура молекул (1937). [12] H. Ulich u. W. Nespital, ZS. f. angew. Chem., 87, 750 (1931).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XXXVIII, № 9

CHEMISTRY

ON THE SYNTHESIS OF ETHYLENE COMPLEXES OF PLATINUM WITH FOUR DIFFERENT SUBSTITUTING GROUPS IN THE INNER SPHERE

By ANNA GELMAN

(Communicated by V. G. Chlopin, Member of the Academy, 9. XII. 1942)

In a former paper([1]) it was mentioned that the attempt to obtain a platinum ethylene-ethylenediamine-chloride with a closed ring had failed. Instead of cyclization, in the presence of ethylene or butadine in the inner sphere ethylenediamine formed a bridge between two atoms of platinum.

Such a course of this reaction made it impossible to solve the problem of separating platinum ethylene-ethylenediamine-chloride into optical antipodes.

This made us look for new ways for the synthesis of optically active ethylene complexes of platinum. After a series of new unsuccessful attempts to introduce ethylene into the cation, it was decided to synthesize a complex containing in the anion next to the ethylene three different subsituting groups, viz.

$$[A_1A_2A_3C_2H_4Pt]\,Me.$$

An anion built like that should be optically active, if the platinum in ethylene compounds were similar to tetravalent platinum.

For substituting atoms it was the most simple way to take Br and I. It was supposed to carry out the synthesis according to the following scheme:

$$K\left[\begin{matrix} C_2H_4 & Cl \\ & Pt \\ Cl & Cl \end{matrix}\right] + 2KBr \rightarrow K\left[\begin{matrix} C_2H_4 & Br \\ & Pt \\ Cl & Br \end{matrix}\right] + 2KCl. \qquad (I)$$

$$K\left[\begin{matrix} C_2H_4 & Br \\ & Pt \\ Cl & Br \end{matrix}\right] + 2KI \rightarrow K\left[\begin{matrix} C_2H_4 & Br \\ & Pt \\ Cl & I \end{matrix}\right] + 2KBr. \qquad (II)$$

With this purpose in mind, to 3.25 g of the ammonium Zeise salt, dissolved in 100 cm³ of water, 2.22 g of KBr were added (2 moles of the bromide per 1 mole of the Zeise salt). The solution was heated to boiling and then kept for 3 hrs on a water bath. The next day the solution, though transparent, was filtered and carefully precipitated with ammonium hydroxide.

The supposed course of reactions:

$$K\left[\begin{matrix} C_2H_4 & Cl \\ & Pt \\ Cl & Cl \end{matrix}\right] + 2KBr \rightarrow K\left[\begin{matrix} C_2H_4 & Br \\ & Pt \\ Cl & Br \end{matrix}\right] + 2KCl \qquad (I)$$

$$K\left[\begin{matrix} C_2H_4 & Br \\ & Pt \\ Cl & Br \end{matrix}\right] + NH_3 \rightarrow \left[\begin{matrix} C_2H_4 & Br \\ & Pt \\ Cl & NH_3 \end{matrix}\right] + KBr. \qquad (II)$$

The yellow fine crystalline precipitate was transferred into a Büchner funnel, washed twice with water, then with ether and filtered with suction to dryness. The precipitate was brought to constant weight in a dessicator and then analysed.

Weighed portion:

0.1036 g when ignited with H_2SO_4 yielded 0.0570 g Pt; Pt—55.02%
0.1145 g when ignited with H_2SO_4 yielded 0.0632 g Pt; Pt—55.20%
Calculated for $[NH_3C_2H_4ClBrPt]$, mol. weight 355.60; Pt—54.90%.

Weighed portion:

14.14 mg when ignited yielded CO_2 3.29 mg; C—6.35%
13.23 mg when ignited yilded CO_2 3.18 mg; C—6.56%
Calculated for $[NH_3C_2H_4ClBrPt]$, C—6.74%

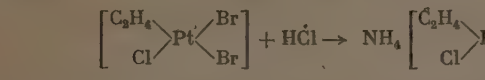
Thus, analysis showed that the reaction had proceeded as expected,

Precipitation with ammonium hydroxide had been carried out with two aims in mind:

1) to isolate (for the first time) a mixed ethylene-ammine-chloride-bromide of platinum;

2) to obtain from it in the most pure state $NH_4[C_2H_4ClBrClPt]$ in order to pass to the iodide that interested us.

For preparing the iodide the chloride-bromide $[C_2H_4NH_3ClBrPt]$ was first converted into an electrolyte according to the equation



In 2 *N* hydrochloric acid the reaction proceeds quite smoothly. An aliquot part of the solution was precipitated with ammonium hydroxide and the yellow precipitate obtained was analysed. Obtained: Pt = 54.87%; calculated for $NH_4[PtC_2H_4ClBrCl]$ 54.90%Pt.

To a solution of $NH_4[PtC_2H_4ClBrCl]$ in the cold an aqueous solution of sodium iodide was added dropwise: 1 mole per 1 mole of the mixed Zeise salt.

At first no change was observed, then slowly gas bulbs began to evolve. On the surface of the solution there appeared a brilliant iridescent film and, finally, there separated a voluminous brown precipitate.

The action of sodium iodide upon the Zeise salt by its outer appearance resembled the action of thiourea upon that salt (2). The brown precipitate has not been carefully investigated as yet.

The reaction of the insertion of iodine into the inner sphere of the Zeise salt was repeated 3—4 times with certain variations, but with invariable results: evolving of ethylene and separation of a brown precipitate.

The one conclusion to be drawn from these facts is that the synthesis of a Zeise salt with three different halogens (Cl, Br, I) by means of the consecutive insertion of Cl, Br and I is impossible; in other words, the attempt to synthesize an anion containing ethylene, capable of optical activity, has failed.

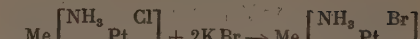
The idea arises that the unstability of the ethylene iodide is connected with the fact that iodine is in a transposition to ethylene. Both substituents—ethylene as well as iodine—have a tendency of forming covalent bonds with the central atom and dispute the place nearest to platinum upon one and the same coordinate.

The synthesis from the Zeise salt of a complex in which iodine and ethylene would be upon different coordinates is theoretically impossible owing to the high *trans*-influence of ethylene, which labilizes the substituting group standing opposite to him, directing the reactions in the inner sphere always in a definite manner.

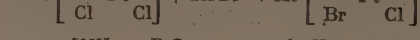
Synthesis of *cis*-$[PtC_2H_4BrNH_3Cl]$. Platinum ethylene-ammine-chloride-bromide has a *trans*-configuration, as it is connected genetically with the Zeise salt (3). For obtaining its *cis*-isomer it is necessary to start from the Kossa salt(3).

Theoretically the following course is possible for the synthesis of the *cis*-isomer.

We succeeded in realizing this course.



(1)



(2)

A solution prepared from 2.1 g of the ammonium Kossa salt +1.41 g KBr+ +100 cm³ of water was slightly acidified with hydrochloric acid and heated for 5 hrs on a water bath. After cooling the solution was filtered and saturated with ethylene.

The next day there separated beautiful brilliant greenish-yellow crystals, quite homogeneous under the microscope. The crystals were filtered off, washed with water, then with ether and dried in a dessicator to constant weight. Analysis gave the following results:

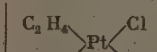
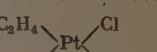
Weighed portion:

0.1148 g when ignited with H_2SO_4 yielded 0.0630 g Pt; Pt—54.88%
0.1124 g when ignited with H_2SO_4 yielded 0.0615 g Pt; Pt—54.72%.
Calculated for [NH_3 ClC_2H_4BrPt], mol. weight 355.60; Pt—54.90%, C—6.74%.

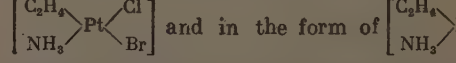
Weighed portion:

12.05 mg when ignited gave CO_2 3.03 mg; C—6.86%
17.09 mg when ignited gave CO_2 4.21 mg; C—6.72%.

Below are tabulated the chief properties of the isomeric platinum ethylene-ammine-chloride-bromides (see table).

Property		
Outer appearance of substance	Beautiful crystals of prismatic form coloured greenish-yellow	Fine crystalline substance coloured yellow
Optical constants	$N_g > 1.783$ $N_p = 1.758$	$N_g = 1.783$ $N_p = 1.708$
Attitude towards hydrochloric acid in the cold	Insoluble	Soluble with the formation of $NH_4[PtC_2H_4ClBrCl]$
Attitude towards silver-nitrate in the cold	First a strong opalescence, then AgBr precipitates	Very feeble opalescence
Solubility in water at 25°C	It was impossible to determine the solubility owing to the easy decomposition of the substance (metallic platinum being separated)	
Solubility in C_2H_5OH at 25° C	Do	

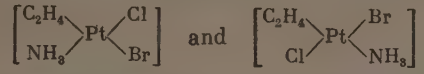
It should be noted that the *cis*-isomer, in its turn, can exist in two forms in the form of the substance mentioned above:



not prepared as yet. We hope to be able later on to find means for its synthesis.

Conclúsions

1) Spatial isomers with four different substituting groups in the inner sphere, one of them being ethylene, have been synthesized for the first time:



2) It has been demonstrated that it is impossible to obtain the anion of a Zeise salt with three different halogens [PtC_2H_4ClBrI], as the introduction of iodine leads to the displacing of ethylene from the complex.

3) The investigation is being continued.

Institute of General and Inorganic Chemistry.
Academy of Sciences of the USSR.

Received
12. XII. 1942.

REFERENCES

[1] A. Gelman, C. R. Acad. Sci. URSS, XXXVIII, No. 8 (1943). [2] А. Гельман, Изв. сект. платины, вып. 14 (1937). [3] И. И. Черняев и А. Д. Гельман, Изв. сект. платины, вып. 15 (1938).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1943. Volume XXXVIII, № 9

PHYSICAL CHEMISTRY

INVESTIGATION OF THE POLYMORPHISM OF TRILAURIN

By G. B. RAVICH and G. G. TZURINOV

(Communicated by V. G. Chlopin, Member of the Academy, 14. XII. 1942)

In working out the problem of the polymorphism of triglycerides the study of the modification of trilaurin has served to a great extent as a basis. This subject has been studied by Grün (1), Othmer (2), Loskit (3), Joglikar and Watson (4), Weigand and Grüntzig (5), Clarkson and Malkin (6). The results obtained by these authors are tabulated below.

Othmer		Loskit		Joglikar and Watson		Weigand and Grüntzig							Clarkson and Malkin		
I	II	I	II	I	III	I			II			III	β	α	γ
						A	B	C	A	B	C	C			
44.3	34	46.4	36.4	46.2	18.0	46.5	46.0	45.0	37.5	37.0	36.0	15	46.4	35.0	15

As may be seen from the table, no agreement has so far been reached as to the number of modifications in trilaurin. Their number, according to different authors, varies from 2 to 7. Clarkson and Malkin's suggestion that the low melting γ-modification (III C, according to the terminology of Weigand and Grüntzig) is vitreous and the conclusion arrived at by Meigand and Grüntzig concerning the presence of a series of intermediate modifications, discovered by none except the above-mentioned authors (IB, IC, IIA and IIB), has aroused particular interest. It should be noted that the discussion about the number of modifications carried on on the pages of Zs. f. anorg. Chem. (1939) has failed to come to positive results, because it was mainly concerned with the comparative reliability of different methods of discovering polymorphism—the microscopic method used by Weigand and Grüntzig and X-ray methods applied in the work of Clarkson and Malkin (who also made microscopic examinations, but these played only a subsidiary rôle). It should be mentioned that the conclusions made by Weigand and Grüntzig were arrived at by using a whole complex of methods and appear therefore to be more reliable. Nevertheless, the problem cannot be looked upon as solved. As a matter of fact, Clarkson and Malkin built their classical thermograms on the basis of only visual observations. One can hardly suppose that under such conditions and at the rates of heating and cooling, usual in the practice of thermal analysis, the thermal effects of melting and transformation of a series of modifications which, moreover, Weigand and Grüntzig believe to proceed in a temperarure interval of but 1.5° C, could be fixed with the necessary accuracy.

All this considered, we thought it essential in studying the problem to have recourse to the method of cooling and heating curves taken by N. S. Kurnakov's

pyrometer, while making use of the differential record, and to subject the modifications to microscopic examination by means of a heating table*. Under a very slow decrease of temperature, achieved by drawing liquid air by drops through the cooling coil, immersed in alcohol serving in its turn as cooling medium for a test-tube with melted tristearin, we obtained thermograms shown on Fig. 1.

The smooth cooling curve was obtained without stirring the melted trilaurin and introducing no crystalline seed into the melt. Both the direct and differential records have fixed only one point of arrest at 35.5° C, i. e. at a temperature near the melting point of the α-phase according to Clarkson and Malkin (35.0°). The heating curve of the substance preliminarily chilled, as described above, to 26°C has a longer arrest at 46.5°, this coinciding with the melting of the β-phase according to Clarkson and Malkin (46.4°). It is easy to draw conclusion that on the slow cooling of the crystallized substance from 35.0 to 26° C (or the subsequent

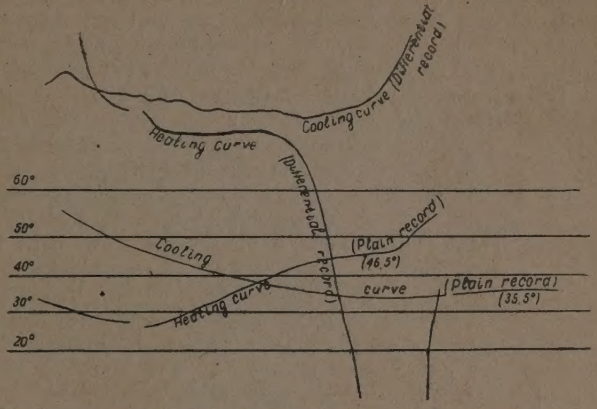


Fig. 1. Thermograms of trilaurin taken on very slow cooling of melt down to 26°C.

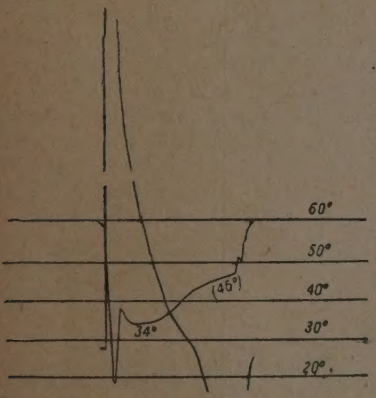


Fig. 2. Thermograms of trilaurin taken on rapid cooling of melt down to 20°C.

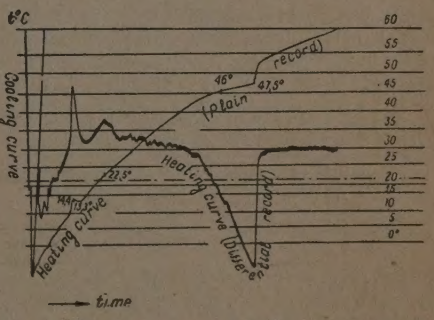


Fig. 3. Thermograms of trilaurin taken on rapid cooling of melt down to —20°C

heating) the transition from the α to the β-phase has taken place, and that only the melting of the latter phase (β) has been fixed on the heating curve.

Under conditions of a very rapid chilling to—20° C (by immersing the test-tube containing the melted trilaurin into alcohol previously cooled by liquid air to—65° C) we obtained thermograms (Fig. 2) with no arrests on the cooling curve. The heating curve points at a sharply noticeable exothermal effect at 34.5°, repeatedly noticed by us in studying the heating curves of tristearin, and corresponding, probably, to a transition of the α-phase near its melting point. The thermogram has

*Microscopic examination was carried out by V. A. Volnova.

also a sloping arrest in the temperature interval 46-47° C, evidently corresponding to the melting of the β-phase, possibly accompanied by side thermal effects. Finally, under conditions of a very rapid chilling of the molten trilaurin to—15° (Fig. 3) a cooling curve was obtained having a sharply noticeable arrest at 20° C, and a heating curve showing a well defined exothermal effect at a temperature about 15° C and the usual effect of the melting of the β-phase within the interval 46—47.5° C. Obviously, under these conditions we were able to fix the transition of the γ-phase and the subsequent effect of the melting of the β-form.

With the kind permission of Prof. A. V. Nikolaev we give, for comparison, a very similar heating curve for boron-sodium-calcite (Fig. 4); the effect 2, according to this author, corresponds to devitrification. It is also very interesting that a microscopical preparation of trilaurin, subjected for many days to as an intense a cooling as that of melted trilaurin in the test-tube (for which purpose a thin layer spread under coverglass on the microscope slide was immersed into mercury chilled previously by liquid air), appears to a naked eye as completely transparent. The data obtained seemed to speak strongly in favour of Clarkson and Malkin's views as to the vitreous state of the γ-form. Yet at the same time we must also give our full support to the observations of Weigand and Grüntzig that the object appears crystalline in polarized light on sufficient magnification (×200). It is therefore very likely that we have here a liquid crystalline state. In this case it is only natural that the liquid phase gives a broad diffuse ring on the powdergrams. On the other hand, under polarized light the anisotropy, inherent to liquid crystals, becomes sufficiently apparent*. Turning to the question of the number of modifications, we find it fit to subscribe to the following point of view. The existence of a γ-form (liquid-crystalline) with the conditional m. p. 15—20° C is beyond doubt. There is no doubt either about the existence of an α-form (m. p. about 35° C) and a β-form (m. p. 46.5° C). As may be seen from Fig. 3, at 46° C the differential curve indicates some very feeble thermal effect, but this necessitates additional checking. At 37° and 37.5° C we were unable to find any thermal effects, and the existence of modifications in this area cannot be confirmed on the basis of the methods used by us (at least under the conditions of chilling the melted trilaurin as described above).

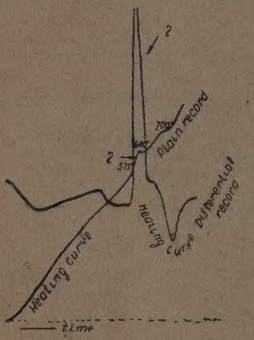


Fig. 4. Devitrification of boron-sodium-calcite according to A. V. Nikolaev.

Institute of General and Inorganic Chemistry.
Academy of Sciences of the USSR.

Received
14. XII. 1942.

REFERENCES

[1] Grün u. Schacht, Ber., **40**, 1770 (1907). [2] Paul Othmer, ZS. f. anorg. Chem., **91**, 209 (1915). [3] K. Loskit, ZS. phys. Chem., **134**, 135 (1928). [4] R. B. Joglikar and H. E. Watson, J. Soc. Chem. Ind., **47**, 365 T (1928). [5] C. Weigand u. W. Grüntzig, ZS. f. anorg. allg. Chem., **206**, 313 (1932). [6] Charles E. Clarkson and Thomas Malkin, Journ. Chem. Soc., London, 666 (1934).

* There still remains room enough to suppose the existence of solid crystals within the resolidified vitreous mass. In this case the former give the effects mentioned microscopically in polarized light, whereas the latter shows itself in the devitrification effect and in others as well. In other words, microscopically we already fix some elements of devitrification, its optimum lying about 20°C and revealing itself in the thermal effect described above.

Prix $ 0.50